

GASEOUS EXPLOSIONS

**Probable Mechanism Causing
Engine Knock**

GEORGE B. WATKINS

**A Thesis submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in the
University of Michigan**

ANN ARBOR

1926



REPRINTED FROM

Industrial *and Engineering* Chemistry

Published by the American Chemical Society

Vol. 19, No. 2

Page 280

February, 1927

Gaseous Explosions¹

III—Effect of Fuel Constitution on Rate of Rise of Pressure

By Geo. Granger Brown and Geo. B. Watkins

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

Apparatus suitable for the quantitative determination of the rate of rise of pressure of a gaseous explosion is described. Normal hexane, heptane, and octane; benzene, toluene, xylene; methyl, ethyl, and amyl alcohols, and ethyl ether were used to prepare explosive mixtures with substantially theoretical oxygen, and nitrogen. These mixtures were exploded under constant initial conditions and the pressure-time curves were graphically differentiated to obtain the maximum rate of rise of pressure. Comparison of the data so obtained indicates that the rate of rise of pressure in a progressive homogeneous reaction (one in which the flame moves progressively through the explosive mixture) increases with molecular weight in the paraffin series, varies inversely with the number of methyl groups added to the benzene ring in the aromatic series, and is about the same for the higher alcohols as for the corresponding paraffin hydrocarbon.

ALTHOUGH a study of the literature reveals many data on the physical and chemical properties of different fuels, and their detonating tendencies in actual engine tests, no quantitative data are available on the rate of rise of pressure of explosions of gaseous mixtures of air and liquid fuels as used in internal combustion engines.

¹ Presented before the Division of Gas and Fuel Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

Nägel² assumed that the velocity of inflammation is of fundamental importance and undertook to measure the velocity of inflammation by an optical pressure recorder or "manograph," and to study the effect of mixture proportions, initial temperature and pressure, upon the rate of inflammation. In his experimental work Nägel used a spherical bomb 40 cm. in diameter, having a capacity of 33.51 liters. It was immersed in a water bath for temperature control, and equipped with a spark gap located at the center of the bomb. On the assumption that complete inflammation is synchronous with maximum pressure, Nägel measured the time required to reach maximum pressure. He worked with hydrogen; Dresden city gas (10% CO, 49% H₂, 27% CH₄, 3% C₂H₄, 0.3% C₆H₆, 3% CO₂, 1% O₂, 6.7% N₂); and producer gas (18.1% H₂, 2.2% CH₄, 0.2% C₂H₄, 18.9% CO, 0.5% C₆H₆, 6.9% CO₂, 0.2% O₂, 53% N₂), submitting curves comparing the rate of rise of pressure of these three fuels. Some of Nägel's results are given in Table I.

Table I—Effect of Fuel Constitution on "Rate of Burning" (Nägel)

FUEL	RELATIVE VOLUME OF GAS IN MIXTURE	IN- ITIAL TEM- PERATURE	IN- ITIAL PRES- SURE	DURATION OF BURNING	MEAN TOTAL VELOCITY OF INFLAMMA- TION	"VER- SUCH" NUMBER
		° C.	Atmos.	Sec.	M./sec.	
Hydrogen	0.2438	15	2	0.0156	12.83	31
Dresden city gas	0.16	15	2	0.0547	3.658	36
Producer gas	0.465	15	2	0.1035	1.627	83

Nägel was not interested in comparing the fuels by rate of rise of pressure but used this means to study the mechanism of flame propagation in gaseous explosion. By scaling the time-pressure curves (numbers 31, 36, 83) published by Nägel, the maximum pressure developed during the explosion is obtained, which, divided by the time in seconds required for the development of the maximum pressure from the instant of spark (called by Nägel the duration of burning) gives the mean rate of rise of pressure of the explosion. Table II shows the results of these calculations.

Woodbury, Lewis, and Canby³ took photographic records of flame travel in explosive mixtures of acetylene, oxygen, and nitrogen, using a cylindrical bomb 4 inches in diameter and 12 inches high, with a spark plug for ignition at the bottom of the bomb. A Midgley indicator mounted at the top of the bomb recorded a time-pressure curve of the explosion on the same time scale as the flame-travel record. As their work included acetylene only, no comparison of different fuels can be made from their data.

Ricardo⁴ submitted time-pressure curves for petrol-air and hydrogen-air explosions in a stagnant mixture taken from the work of Fenning.⁵ In order to compare fuels by means of the rate of rise of pressure during explosion it is absolutely necessary that such measurements be made under identical conditions of initial temperature and density of charge. These requirements Fenning has apparently neglected.

As the "fuel knock" in an internal combustion engine is due to an extremely high rate of rise of pressure in the explosion, quantitative measurements of the rate of rise of pressure accompanying explosions of gaseous mixtures of

² *Mitt. Forschungsarbeiten*, **54**, 1 (1908).

³ *J. Soc. Automotive Eng.*, **8**, 209 (1921).

⁴ *J. Roy. Aeronautical Soc.*, **28**, 49 (1924).

⁵ Reports and Memoirs, No. 902 (April, 1924), No. 979 (1925).

oxygen and nitrogen with different liquid fuels, as used in internal combustion engines, are necessary before the mechanism of engine knock, sometimes referred to as detonation, can be understood.

Table II—Mean Rate of Rise of Pressure Determined from Nügel's Data

FUEL	MAX. PRESSURE DEVELOPED	DURATION OF BURNING	MEAN RATE OF RISE OF PRESSURE
	<i>Lbs./sq. in.</i>	<i>Sec.</i>	<i>Lbs./sq. in./sec.</i>
Hydrogen	190	0.0156	12,150
Dresden city gas	187	0.0547	3,420
Producer gas	171	0.1035	1,650

Apparatus

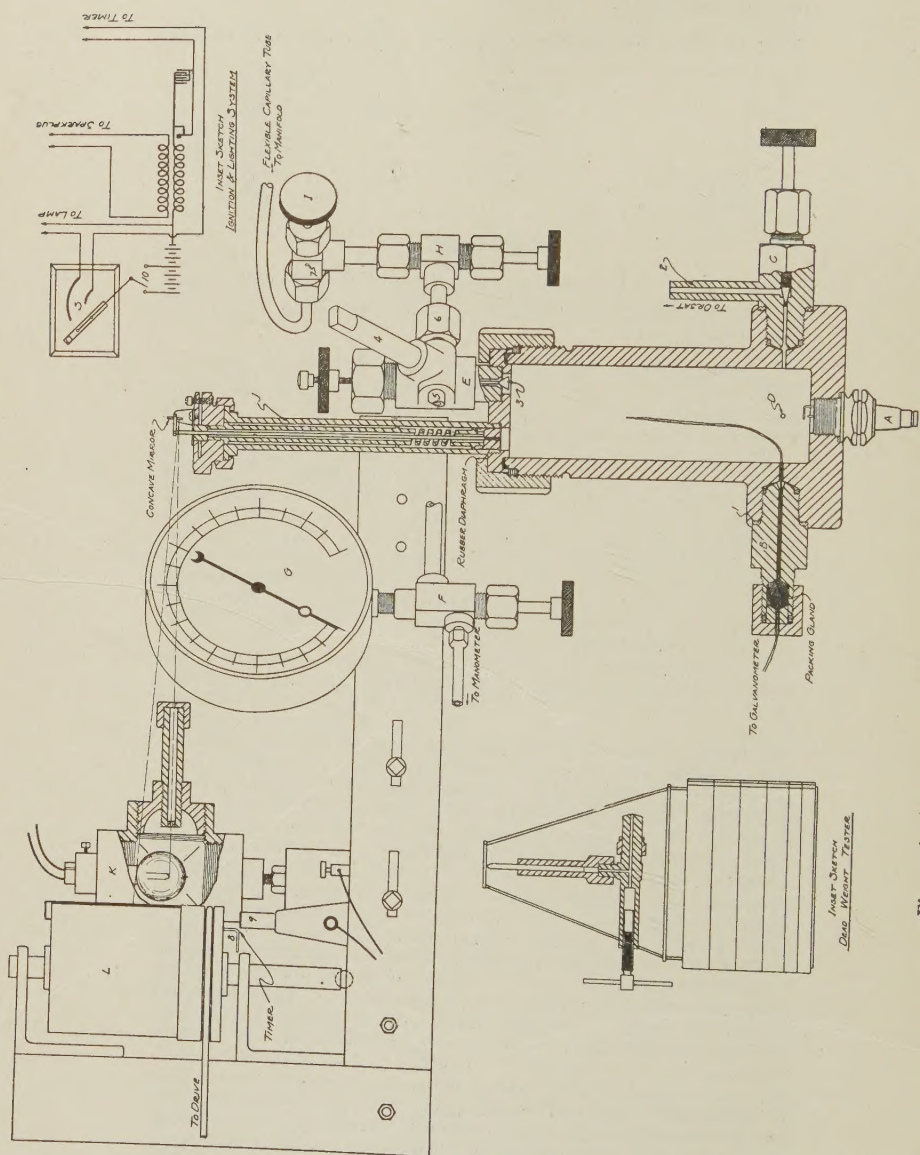
For this work a bomb was developed similar to that used by Brown, Leslie, and Hunn⁶ but incorporating many improvements.

EXPLOSION BOMB—The explosion bomb (Figure 1), 6.99 cm. (2.75 inches) in diameter and about 17.8 cm. (7 inches) long, having a capacity of 395 cc., was machined from steel bar stock and assembled with specially made, high-pressure valves and fittings.

The sparking plug, *A*, located centrally in the bottom of the bomb, is a $\frac{7}{8}$ -inch S. A. E. standard A-C plug. The female fitting for the spark plug was recessed by milling, and the shoulder grooved, so that by using an annealed copper washer on the shoulder of the spark plug very little pressure was required to make the joint gas-tight. The terminals of the plug were maintained at $\frac{1}{32}$ (0.03125) of an inch throughout the experimental work, and were just flush with the inside surfaces of the bomb. The igniting spark was obtained from a Ford spark coil, using 12 volts in the primary circuit.

The thermocouple for recording the initial temperature of the explosive charge was introduced through the side and at the bottom of the bomb, by means of a packing plug, *B*, so that the hot junction of the couple was in the approximate center of the combustion chamber. The packing plug for the thermocouple was machined from hexagon brass stock, having a capillary bore from the end of the plug that screwed into the bomb to the packing gland. The thermocouple wires were insulated in the capillary end of the packing plug with a double bore usalite tube which extended out to the packing gland. From this point the insulation was continued for several inches with narrow strips of tire tape and asbestos cord. A nodule of asbestos cord was made of sufficient size just to fill the packing gland around the insulated wires. A centrally bored brass slug was then forced on the nodule of asbestos in the packing gland by a cap screw, making a perfectly gas-tight joint. The female fitting for the packing plug was drilled and tapped with a $\frac{7}{8}$ -inch S. A. E. standard thread to within $\frac{1}{4}$ of an inch of the combustion chamber, leaving a round seat which was connected to the combustion chamber by a capillary bore. A recess, *1*, was milled on the outside of the female fitting and the shoulder grooved for the purpose of gasketing. The end of the packing plug screwing into the bomb was of greater curvature than the seat in the bomb fitting, so that a gas-tight joint would be insured when contact was made. To insure still further the tightness of the joint, a shoulder was cut and grooved on the packing plug just to fit the recess, *1*, milled on the female fitting. The length of the thread end of the packing plug was 0.004 of an inch greater than the distance from the shoulder to seat in the bomb fitting, so that by placing

⁶ THIS JOURNAL, 17, 397 (1925).



a $\frac{1}{16}$ -inch lead washer against the shoulder of the packing plug, which was then tightened in the fitting until contact was made at its seat, a perfectly gas-tight joint was obtained.

The release valve, *C*, located at the side and bottom of the bomb, was machined from hexagon brass stock, and had the same construction for fitting the bomb as the packing plug described above. The arm of the release valve was connected to the valve body by means of a screw fitting and silver solder. A flexible capillary tube, connected to the other end of the arm, 2, by means of a ball and socket joint, led through the wall of the dark room to the gas analysis apparatus at *a*, Figure 2.

The packing glands for the release valve and all other needle valves were of the standard type shown in the cross section of the packing plug, *B*. The valve stems for all needle valves were machined from $\frac{1}{8}$ -inch drill rod and threaded.

The fitting, *D*, at the side and bottom of the bomb, was used for dead-weight calibration of the pressure indicator. During the operation of the bomb this opening was made gas-tight by means of a brass plug having the same construction for the bomb fitting as that of the packing plug.

The dead-weight tester is shown in cross section with calibrated weights, in inset sketch.

The charging valve, *E*, connected to the bomb through the cover plate, was machined from brass, cast in the form of a 45 degree lateral. The female fitting for the charging valve was drilled and tapped with a $\frac{7}{8}$ -inch S. A. E. standard thread, leaving a shoulder of metal $\frac{3}{16}$ inch wide and $\frac{3}{16}$ inch thick. The shoulder was grooved and gasketed with an annealed copper washer, which made a gas-tight joint with the charging valve in position.

The main body part of the valve was centrally bored and fitted with a steel rod machined and threaded so as to give a cone-shaped, inverted needle valve, seating at the bottom where the valve enters the bomb, 3. The opening and closing of the valve was controlled by a solid brass wheel threaded to fit the valve stem, and resting on top of the cap screw. This valve made it possible to shut off the bomb from all connections during the explosion.

The lateral branch of the valve was centrally bored down to the main chamber of the valve, then drilled, tapped, and fitted with a brass plug, 4. The removal of this plug for charging the liquid fuel was the only joint on the apparatus that had to be broken in charging the bomb. Two projections, 5 and 6, one on each side of the lateral branch, above the base and at right angles to the plane of the lateral, were centrally bored, so that they connected to the central bore of the lateral and thence into the main chamber of the valve. A capillary brass nipple, taking off from the lateral projection, 5, with a ball and socket joint, was connected to needle valve, *F*, below the valve seat with a screw fitting and metallic seat. The connection opened to a standard Bourdon gage, *G*, connected to, but not controlled by, the needle valve, *F*. A flexible capillary lead was connected to the needle valve, *F*, above the valve seat, and led to a mercury manometer stationed on the wall of the dark room. A capillary brass nipple taking off from the lateral projection, 6, with a ball and socket joint, was connected to needle valve, *H*, above its seat with a screw fitting and metallic seat.

Needle valve, *H*, below its valve seat, was connected to needle valve, *I*, below its valve seat, by a capillary brass nipple with screw fittings and metallic seats. A flexible capillary tube leading from a common manifold used for charging oxygen and nitrogen, was connected to needle valve, *I*, below its valve seat with a ball and socket joint. The needle valve, *I*, was supplied with an opening above its valve seat, 7, for flushing the line before charging the bomb.

PRESSURE ELEMENT—For recording time-pressure curves of the explosions a modified Midgley indicator was used. The pressure element, *J*, similar to that described by Midgley,⁷ was mounted in the cover plate of the bomb. The female fitting for the pressure element was drilled and tapped with a $\frac{7}{8}$ -inch S. A. E. standard thread, leaving a shoulder approximately $\frac{1}{8}$ inch wide and $\frac{1}{8}$ inch thick to support the circular rubber diaphragm, cut from Gooch crucible tubing, which was necessary to prevent the gases escaping around the piston of the indicator. The rubber gasket was carefully placed in position, resting on the shoulder of the female fitting, and the pressure element screwed down fairly tightly to hold the gasket in place. This construction produced a joint that remained gas-tight for three or four runs.

The split steel tube connecting the push rod of the indicator spring with the rotating axis of the concave mirror on top of the pressure element gave considerable play on continued use, and was replaced by a solid steel arm. The arm was drilled at one end to fit the rotating axis of the mirror and held rigidly in position by a small set screw. The other end of the mirror arm was connected to the push rod by means of a ball and socket joint, constructed by milling a slot in the end of the mirror arm so that the ball on top of the push rod could be sprung into its seat in the sides of the milled slot. This construction served to actuate the concave mirror with a minimum vibration, so that relatively smooth time-pressure curves of the explosions could be obtained.

LIGHTING SYSTEM—The camera box which is standard equipment for the Midgley indicator was discarded after the experimental work was begun because of the unsatisfactory time-pressure curves obtained due to excessive vibration of the camera box, lack of parallelism in the revolving octagon mirror, and the smudging of the prints by the reflection of the photographic light beam from the surface of the curved glass in the front of the box against which the photographic paper was placed.

The lighting system that was finally developed for this work was essentially a source of light coming from the lamp box, *K*, impinged upon the concave mirror mounted on top of the pressure element, and reflected from the concave mirror on a revolving drum, *L*.

The source of light was a 50-candle-power automobile head lamp mounted in the box, *K*. The lamp box was made from a $1\frac{1}{2}$ -inch pipe cross, closed with pipe plugs and painted with aluminum paint so as to give better reflection. The front plug, through which the light was emitted, was drilled, tapped, and fitted with a $\frac{1}{2}$ inch by $3\frac{1}{2}$ inch small-bore steel tube. The end of the tube nearer the lamp was tapped and fitted with a small brass plug of capillary bore to control the amount of light emitted. The outer end of the tube was threaded to fit $\frac{1}{4}$ -inch pipe caps, which served as shutters to control further the light emitted, by varying the aperture of the pipe caps. The top plug was centrally drilled for the lamp socket, which was held firmly in position by a set screw in the top of the plug and at right angles to the lamp socket. The bottom plug of the lamp box was drilled, tapped, and fitted with a $\frac{3}{8}$ -inch, solid iron nipple. The whole was mounted on the base of the revolving drum by means of an angle iron with milled slots, so that the light could be moved forward and backward and through any angle, at will.

REVOLVING DRUM—The revolving drum, *L*, was made from an aluminum casting, centrally bored, pressed on an arbor and machined in a lathe, between centers. At the lower end of the drum a V-shaped groove was machined for the belt drive.

A curved steel wire was pressed into a hole drilled in the bottom of the drum, 8. The wire extended down a short distance from the bottom of the drum and then bent horizontally in the arc

⁷ *J. Soc. Automotive Eng.*, 7, 491 (1920).

of a circle with its center on the axis of the drum. A piece of brass spring, 9, was fastened to, and insulated from, the base support of the revolving drum. The spring was so placed as to make contact with the steel wire as the drum revolved. This arrangement served as a timing device for controlling the spark.

The photographic paper was held in position by wrapping the paper around the drum and placing the overlapping ends under a spring steel wire fastened to the top and bottom of the drum.

The ignition and lighting system, shown diagrammatically in the inset sketch, Figure 1, was operated by two 6-volt batteries. These were connected so that by throwing the switch, 10, either to right or left, 6 or 12 volts would be impressed on the light and the primary circuit of the spark coil. During all runs it was necessary to use the higher voltage to give sufficient intensity of light to affect the photographic paper. The 6-volt circuit was used for setting and focusing the light, and for calibrating the pressure indicator with the dead weight tester. The contact bar

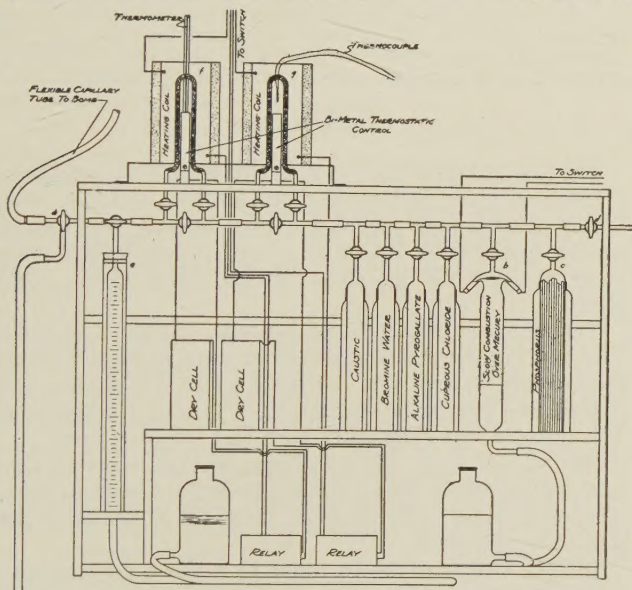


Figure 2—Gas Analysis Apparatus

connecting the switch, *S*, with the lamp circuit was longer than the one connecting the ignition circuit, so as the switch, *S*, was manually moved in clockwise direction, the filament of the lamp would be up to intensity before the charge was fired.

GAS ANALYSIS—The apparatus shown in Figure 2 was designed so that complete analyses could be made of the products of combustion from the explosion in the bomb. The Hankus type of pipet⁸ was used for the absorbing reagents, with a capillary cross blown on the top. The capillary crosses were lined up and connected with Scimatco rubber tubing so that the dead space above the pipets was decreased to a minimum. The slow combustion pipet, *b*, was designed with two lateral openings diametrically opposite. A resistance coil was placed in the pipet, with its terminals resting on the opposite shoulders. The lateral openings were closed with rubber stoppers having copper leads through their centers. By raising the leveling bottle the arms were filled with mercury and contact made.

⁸ *Chem. & Met. Eng.*, 9, 302 (1911).

to The phosphorus pipet, *c*, was of greater capacity than the one just described, and was placed at the end of the line. This arrangement made it possible to flush out the entire line with nitrogen, preliminary to a gas analysis.

The resistance furnaces, *f* and *g*, were constructed by winding a coil of chromel-A wire on a waxed cardboard cylinder. Alundum cement was then molded around the cylinder, making a $1\frac{1}{2}$ -inch wall of insulation. After the cement had thoroughly set, the furnaces were heated up and the cardboard cylinder removed. The furnaces were wrapped with asbestos paper and mounted $1\frac{1}{2}$ inches from the frame of the apparatus, on galvanized sheet iron. Circular holes were cut in the galvanized iron beneath each furnace for the passage of the copper oxide combustion tubes and the bimetal thermostats. The thermostats controlled the temperature of the furnaces, by operating relays controlling the supply of current.

The copper oxide combustion tubes were made in the form of a U, from Pyrex tubing filled with copper oxide, and centered in the resistance furnaces. They were connected into the line with glass capillary manifolds, provided with stopcocks. This made it possible to by-pass one or both of the furnaces at any time.

Fuels Studied

The four classes of fuels used in this work were paraffin hydrocarbons, aromatic hydrocarbons, alcohols, and ethyl ether.

The paraffin fuels included normal hexane, heptane, and octane, prepared by Brown and Carr⁹ by carefully fractionating straight-run gasoline distilled from Cabin Creek crude.

The aromatic fuels included benzene, toluene, and xylene. The two latter were obtained from the Chemical Stores of the University, and were not quite pure. Distillation analyses showed them to be about 99 and 98 per cent, respectively. The benzene was chemically pure and thiophen free.

The alcohol fuels, which included methyl, absolute ethyl, and amyl alcohols, were obtained from the Chemical Stores. The ethyl ether, also obtained from the Chemical Stores, was chemically pure.

INITIAL CONDITIONS—In order to make a comparison of fuels on the basis of the rate of rise of pressure during combustion, it is necessary to have all of the initial conditions of the experiments the same for every fuel.

The initial density of the gases was the same in every determination, that is, a sufficient amount of fuel was charged into the bomb to give a theoretical mixture with an absolute pressure of oxygen equal to 1050 mm. of mercury at 25° C. The oxygen charged was measured with a mercury manometer, and the mixture strength was verified by complete analyses of the products of combustion.

The amount of nitrogen added to every explosive mixture was the same, and was measured with a Bourdon type of pressure gage. The absolute amount of nitrogen varied with the barometric pressure during the experimental work, as the products of combustion were always swept from the bomb with nitrogen. This variation in nitrogen throughout

⁹ THIS JOURNAL, 18, 718 (1926).

the entire experimental work was less than 0.8 per cent, which was within the accuracy of the pressure gage readings.

The initial pressure of combustion varied somewhat with the different classes of fuels used, and in accord with the number of molecules of the different fuels required to give a theoretical mixture with the absolute amount of oxygen used.

The initial temperature of combustion was maintained constant at 140° C. through the experimental work.

Calibration

PIPET—The pipet used for charging the fuels into the bomb was made from a 1-cc. capillary-bore pipet. It was calibrated to read 0.01 cc. and could be estimated at 0.005 cc. The charging end of the pipet was drawn out so that it could be introduced into the capillary bore of the charging valve (Figure 1). In this way the fuel was charged directly into the main bore of the charging valve.

PRESSURE ELEMENT—Before the experimental work it was necessary to calibrate the pressure element in order to measure the magnitude of pressure rise during the explosion, in absolute terms. The dead-weight tester shown in cross section in inset (Figure 1) was fitted to the bomb at *D* after removing the brass plug. The piston supporting the weights of the tester was held in a vertical position by screwing the lock-nut against the shoulder of the female fitting of the bomb. Then, with the charging valve open, the pressure element was removed from the cover plate and the bomb and screw cylinder of the dead-weight tester filled with glycerol. The rubber diaphragm was inserted and the pressure element screwed back in position. The beam of light was focused near the base in an axial plane of the rotating drum.

The charging valve was now closed, leaving the bomb filled with glycerol under atmospheric pressure. The room was made dark and a piece of bromide photographic paper fastened around the rotating drum. The drum was then set in motion, and the switch, *S*, controlling the indicator light closed for an instant, giving the base line at atmospheric pressure. Calibrated weights were now loaded on the tester, and the screw plunger turned until the weight on the tester was balanced by the pressure of the glycerol, when the switch controlling the indicator light was again closed, giving another point on the calibration curve.

The calibration data are given in Table III.

Table III—Calibration of Optical Pressure Indicator

GAGE	VERTICAL DISTANCE ON PHOTOGRAPHIC PAPER	
	Increasing pressure	Decreasing pressure
<i>Lbs./sq. in.</i>	<i>Inches</i>	<i>Inches</i>
115	0.330	0.330
218	0.640	0.640
320	0.960	0.960
422	1.295	1.295
522	1.605	1.605
625	1.950	1.950

The calibration of the pressure element was continued in this way by loading the tester with calibrated weights, until about 600 pounds per square inch above atmospheric pressure was reached. Then the exposed photographic paper was replaced by another and the calibration repeated in the reverse order. The results proved that the indicator spring behaved the same when subjected to loading as it did when the load was released. After the experimental work was completed, the pressure element was again calibrated in the same manner, and was found to have the same calibration.

Operation

Before each run, the products of combustion from the previous explosion were completely swept from the bomb with nitrogen. This was accomplished by opening the charging valve and alternately charging the bomb with nitrogen to 80 pounds per square inch gage and releasing the pressure, for five times, while the temperature of the bomb was well above 100° C. The bomb was cooled to 25° C. and again swept with nitrogen in the manner just described. Then with the release valve slightly open at the bottom of the bomb, the brass plug was removed from the charging valve and the desired amount of fuel charged into the bomb by means of the calibrated pipet. The brass plug was quickly screwed into place and the release valve closed.

With valve *H* closed and valve *I* open, the charging manifold and flexible capillary lead were flushed out with oxygen. Valve *I* was then closed and about 20 pounds per square inch gage pressure of oxygen were charged into the bomb through valve *H*. Valve *F* was opened, connecting the manometer to the bomb and, by carefully controlling valve *H*, exactly 1050 mm. pressure of oxygen was charged. The manometer was disconnected from the bomb by closing valve *F*, and, after flushing the charging manifold and flexible lead, nitrogen was charged to 56 pounds per square inch gage. The gas burners were adjusted and the temperature of the mixture slowly raised to 155° C., as indicated by the thermocouple in the bomb. The gas burners were then turned out, and the mixture allowed to cool to 140° C. During this cooling period the room was darkened, and photographic paper was placed in position on the drum. The motor driving the drum was started, and the light switch, 10, thrown to the left to connect the 12-volt circuit.

When the temperature had fallen to 140° C. the pressure in the bomb was recorded, the charging valve closed, and the charge fired by manually moving the switch, *S*, in a clockwise direction. The motor driving the drum was stopped and the exposed photographic paper removed from the drum and developed. The temperature and pressure of the combustion products were recorded.

The release valve at the bottom of the bomb was opened and the flexible capillary tube leading to the gas analysis

apparatus was flushed out with the products of combustion. A sample was then collected, measured, and analyzed.

In making the analyses of the combustion products the carbon dioxide was determined by absorption in the sodium hydroxide pipet, the unsaturated hydrocarbons in the bromine pipet, and the oxygen in the phosphorus pipet. The carbon monoxide was determined by absorption in the acid cuprous chloride pipet, rather than with the copper oxide furnace. The reason for the choice of this method was twofold: (1) it consumed less time than the combustion method, and (2) on comparing the results obtained by the two methods on the same sample of gas, the fresh acid cuprous chloride was found to give slightly higher values for carbon monoxide. The above results are in agreement with the results of Ott and Deringer.¹⁰ These investigators found that the simultaneous determination of carbon monoxide and hydrogen by fractional combustion over copper oxide at 300° C. always gave low values for carbon monoxide and high values for hydrogen, while the determination of carbon monoxide by absorption in acid cuprous chloride solution and by combustion over platinum gave consistent and accurate results.

The hydrogen and methane were oxidized by passing the gas through the copper oxide furnaces in series. The amount of each was determined by measuring the contraction and the carbon dioxide formed.

The rotating drum was driven at a speed of 1365 r. p. m., determined by a revolution counter, throughout the experimental work. The horizontal distance on the time-pressure curves was 25.1 cm. (9.89 inches). From these data the time required for the light to travel horizontally was calculated to be 0.00179 seconds per centimeter or 0.00456 seconds per inch. The figures showing the time-pressure curves of the explosions have for their zero ordinate the initial pressure of the fuel mixture. The zero abscissa is taken at the instant of recorded pressure rise. These figures were plotted by scaling the original photographic curves according to the calibration of the pressure element and the time scale as calculated.

The derived curves showing the rate of rise of pressure, dP/dt , were drawn by graphically differentiating the time-pressure curves according to the method given by Running.¹¹ The average rate of rise of pressure was calculated by dividing the maximum pressure recorded by the time in seconds required for its development.

Results

Figure 3 shows a time-pressure curve, P , from an explosion of a mixture of oxygen, nitrogen, and normal octane. This curve was differentiated by drawing horizontal lines 1-2, 3-4, 5-6, etc., so that the area under these lines is numerically

¹⁰ *J. Gasbel.*, **63** (1920), Nos. 13, 14, 16, and 17.

¹¹ *Mich. Technic*, **32**, 41 (1919); also *Lefax*, October, 1920, pp. 1-4.

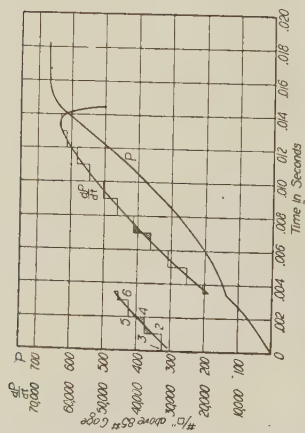


Figure 3—Time-Pressure Curve and Rate of Rise of Pressure of Normal Octane—Run 141

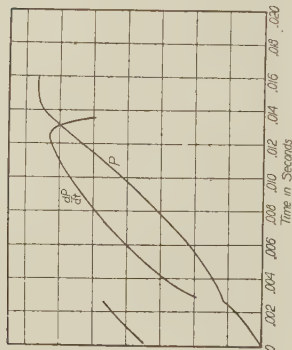


Figure 4—Time-Pressure Curve and Rate of Rise of Pressure of Benzene—Run 148

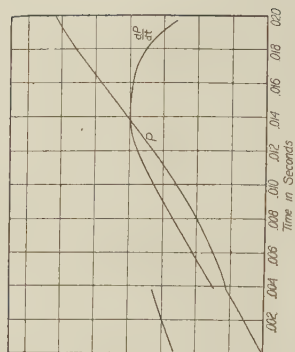


Figure 5—Time-Pressure Curve and Rate of Rise of Pressure of Absolute Alcohol—Run 153

equal to the difference in ordinates of the integral curve, P . A smooth curve, dP/dt , was drawn through these horizontal lines so that the area under the curve is the same as the area under the horizontal lines. This can be done by drawing the derived curve, dP/dt , so that the area above the curve and below the horizontal line is equal to the area below the curve and above the horizontal line, as indicated by the shaded areas between 3-4.

The method of obtaining the derived curves is theoretically accurate, and the derived curves so obtained are subject to the errors of mechanical drawing only.

Figure 4 shows a time-pressure curve, P , and the rate of rise of pressure in pounds per square inch per second, as the derived curve (dP/dt), from a similar explosive mixture containing benzene. Figure 5 shows the corresponding curves from a similar explosive mixture containing absolute ethyl alcohol.

Table IV gives the fuels used, the density of charge, the amount of inert nitrogen in the explosive mixture, and the initial conditions of the experiment.

Table IV—Initial Conditions of Explosive Mixtures

RUN	FUEL	ATMOS- PHERE PRES- SURE	WEIGHT OF FUEL	FIRE, GAGE	IGNITION PHENOMENA
		<i>Mm. Hg</i>	<i>Grams</i>	<i>Lbs./sq. in.</i>	
150	<i>n</i> -Hexane	742	0.2025	84	Whistle
153	<i>n</i> -Heptane	739	0.2068	84	Whistle
141	<i>n</i> -Octane	744	0.2279	83	Whistle
148	Benzene	744	0.2285	84	Whistle
194	Toluene	740	0.2442	84	Whistle
179	Xylene	743	0.2924	85	Whistle
175	Methanol	735	0.5033	96	Whistle
158	Absolute alcohol	738	0.3629	85	Whistle
182	Amyl alcohol	743	0.2934	85.5	Whistle
201	Ether	745	0.2761	88	Click

Initial gas in bomb, nitrogen.

Temperature charged, 25° C.

Partial pressure: oxygen charged, 21 pounds per square inch; nitrogen charged, 35 pounds per square inch.

Temperature fired, 140° C.

Table V gives the fuels used, with corresponding run numbers; the physical properties of the fuels; the maximum pressure developed; the time in seconds required for the development of maximum pressure; the maximum rate of rise of pressure taken from the derived curve; the average rate of rise of pressure obtained by dividing the maximum pressure developed by the time in seconds required for its development; and the analysis of the combustion products. At the bottom of Table V are given the results and averages of four different runs on toluene. In all cases from two to six checks were made on each fuel, the checks being compared by superimposing the time-pressure curves, while wet, and comparing the analyses of the combustion products. In all cases other than toluene, the time-pressure curves of the check runs were identical when compared in this way, so that no averages were necessary with these fuels.

Table V—Fuel Constitution and Rate of Rise of Pressure

RUN	FUEL	BOILING POINT RANGE OF FUEL	SPECIFIC GRAVITY	MAX. PRES- SURE	TIME FOR MAX. PRES- SURE	RATE RISE OF PRESSURE		ANALYSES OF PRODUCTS OF COMBUSTION							
						MAX. $\frac{dP}{dt}$	AV. $\frac{dP}{dt}$								
						$Lbs./sq. in.$	$Lbs./sq. in./sec.$	CO_2	C_nH_{2n}	O_2	CO	H_2	CH_4	N_2	
		$^{\circ}C.$		$Lbs./sq. in.$	$Sec.$			%	%	%	%	%	%	%	%
150	n-Hexane	67-57.6	0.6639(29/15)	675	0.0195	47,500	34,600	17.0	0.0	1.5	1.8	2.1	0.1	77.5	
153	n-Heptane	98.7-98.9	0.6893(29/30)	655	0.0175	61,500	37,400	18.9	0.0	1.2	1.3	1.2	0.3	77.1	
141	n-Octane	124-124.3	0.7123(29/30)	668	0.0165	63,700	40,550	19.7	0.0	1.5	0.2	1.1	0.1	77.4	
148	Benzene	80.36	0.879(29/30)	665	0.0153	63,000	43,400	21.6	0.2	1.4	0.9	0.4	0.0	75.5	
194	Toluene	(99%)111	0.8598(25/15)	650	0.0170	56,500	38,200	22.0	0.0	1.8	1.4	0.9	0.4	73.5	
179	Xylene	(98%)139	0.860(25/15)	675	0.0190	47,000	35,500	21.3	0.2	1.3	1.3	0.8	0.1	75.0	
175	Methanol	65-67	0.7864(25/15)	705	0.0195	52,000	36,100	18.4	0.0	1.6	1.4	1.8	0.0	76.8	
158	Ethyl alcohol	78.4	0.789(29/30)	650	0.021	39,500	30,900	19.0	0.0	1.3	0.6	0.7	0.1	78.3	
182	Amyl alcohol	127-131	0.815(25/30)	675	0.020	48,000	33,700	19.5	0.0	2.1	0.2	1.4	0.2	76.6	
201	Ethyl ether	35	0.719(15/4)	665	0.01375	>200,000	48,400	18.5	0.0	1.3	0.1	0.4	0.0	79.7	
136	Toluene	(99%)111	0.8598(25/15)	675	0.018	55,000	37,500	22.3	0.0	1.6	0.2	0.8	0.2	74.9	
143	Toluene	(99%)111	0.8598(25/15)	660	0.017	57,000	38,800	22.2	0.0	1.9	1.4	1.3	0.0	73.0	
193	Toluene	(99%)111	0.8598(25/15)	650	0.017	56,000	38,200	22.0	0.0	1.8	1.4	0.9	0.4	73.5	
194	Toluene	(99%)111	0.8598(25/15)	650	0.017	56,500	38,200	22.0	0.0	1.8	1.4	0.9	0.4	73.5	
AVERAGE				659		56,125	38,175								

Conclusions

Comparison of the data reported in Table V indicates that, at least with the fuels tested, the rate of rise of pressure in a progressive homogeneous reaction

1—Increases with molecular weight in the paraffin series.

2—Varies inversely with the number of methyl groups added to the benzene ring in the aromatic series.

3—Is approximately the same for normal octane and benzene; for normal heptane and toluene; and for normal hexane and xylene.

4—Is about the same for the higher alcohols as for the corresponding paraffin hydrocarbons.

5—Is exceedingly rapid for ether.

It is well known that the aromatic hydrocarbons do not "knock" in internal combustion engines so readily as do the paraffin hydrocarbons. When the data reported in this paper are interpreted with this fact in mind, it is evident that the rate of rise of pressure in a progressive homogeneous explosion cannot be the sole factor determining the tendency of a fuel to knock in an internal combustion engine. The same conclusion is suggested by data previously reported on the effect of initial temperature on the rate of rise of pressure.⁶ A later paper will suggest another factor which, taken into consideration with the rate of rise of pressure, is adequate to explain engine knocking.

REPRINTED FROM

Industrial and Engineering Chemistry

Published by the American Chemical Society

Vol. 19, No. 3

Page 363

March, 1927

Gaseous Explosions¹

IV—Rate of Rise of Pressure, Velocity of Flame Travel, and the Detonation Wave

By Geo. Granger Brown and Geo. B. Watkins

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

Velocity of flame travel and rate of rise of pressure are shown to be similar and vary in the same way with changing initial conditions.

Detonating mixtures of pure liquid fuels and substantially theoretical oxygen were exploded with varying amounts of nitrogen in the constant volume bomb. The amount of nitrogen necessary to reduce the intensity of the detonation to an arbitrary standard was found to vary directly as the rate of rise of pressure as reported in the previous paper. These data lead to the conclusion that the rate of rise of pressure upon explosion of a fuel mixture is the major factor indicating the tendency of that fuel mixture to set up the detonation wave in a progressive homogeneous reaction, and that engine knock is not due to a detonation wave as recognized in progressive homogeneous explosions.

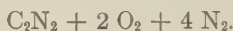
THE addition of a diluent to any reactive mixture generally decreases the rate of the reaction. If the foreign material increases the rate of the reaction or has an abnormal effect in decreasing the rate of reaction, the foreign material is called a catalyst. Gaseous explosions are chemical reactions, and are affected by diluents and catalysts in the same way as other chemical reactions.

It is impossible to measure directly the rate of reaction in

¹ Presented under the title "Gaseous Explosions. IV—Rate of Rise of Pressure and the Detonation Wave" before the Division of Gas and Fuel Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

any progressive gaseous explosion (one in which the flame moves progressively through the explosive mixture).² The effect of diluents on the velocity of the detonation wave was accurately determined by Dixon³ in detonating mixtures containing hydrogen, methane, ethylene, acetylene, carbon monoxide, and cyanogen. In every case the addition of a diluent, either oxygen or nitrogen, decreased the velocity of the detonation wave. The data reported by Dixon, showing the effect of nitrogen and oxygen as diluents on the velocity of the detonation wave in explosive mixtures of hydrogen and oxygen, are plotted in Figure 1.

Dixon also found that the detonation wave was not uniformly propagated in mixtures of methane, oxygen, and nitrogen in the proportion $\text{CH}_4 + 1.5 \text{ O}_2 + 2.5 \text{ N}_2$. Berthelot⁴ found it impossible to initiate the detonation wave in mixtures of carbon monoxide or of methane and air under atmospheric pressure, and in cyanogen mixtures of the composition



Both of these investigators found that mixtures of hydrogen and air propagated the detonation wave readily. These meager results which are reported in Table I seem to indicate that the amount of nitrogen per unit volume of reactants necessary to prevent propagation of the detonation wave varies as the velocity of the detonation wave propagated in similar mixtures free from the nitrogen diluent.

Diluents Decrease Velocity of Flame and Rise of Pressure

Since the classic work of Dixon, many investigators have studied the effect of diluents on flame propagation and rate of rise of pressure in gaseous explosions.

Table I—Effect of Nitrogen on Initiation of Detonation Wave

FUEL MIXTURES	VELOCITY	
	Dixon	Berthelot
	<i>M./sec.</i>	<i>M./sec.</i>
2 H ₂ + O ₂	2821	2810
2 H ₂ + O ₂ + 7 N ₂	Presumably not propagated	
CH ₄ + 2 O ₂	2322	
CH ₄ + 2 O ₂ + 7.5 N ₂		Not propagated
CH ₄ + 1.5 O ₂	2470	
CH ₄ + 1.5 O ₂ + 2.5 N ₂	Went out sometimes	
C ₂ N ₂ + 2 O ₂	2321	
C ₂ N ₂ + 2 O ₂ + 4 N ₂		Not propagated
2 CO + O ₂	1930 extrapolated	1940 calculated
2 CO + O ₂ + 4 N ₂		Not propagated

Mason and Wheeler,⁵ and later Payman,⁶ found that when nitrogen was added to explosive mixtures of methane and

² Brown, *THIS JOURNAL*, **17**, 1229 (1925).

³ *Trans. Roy. Soc. London*, **184A**, 97 (1893).

⁴ *Compt. rend.*, **93**, 18, 145 (1881).

⁵ *J. Chem. Soc. (London)*, **111**, 1044 (1917).

⁶ *Ibid.*, **117**, 43 (1920).

oxygen it decreased the velocity of flame propagation before the detonation wave was initiated, as Dixon found that nitrogen decreased the velocity of flame propagation in the detonation wave. Some of these data are given in Table II. Similar results were obtained by Campbell and Ellis,⁷ who found that the addition of nitrogen to explosive mixtures of methane, ethylene, and carbon disulfide decreased the velocity of flame travel.

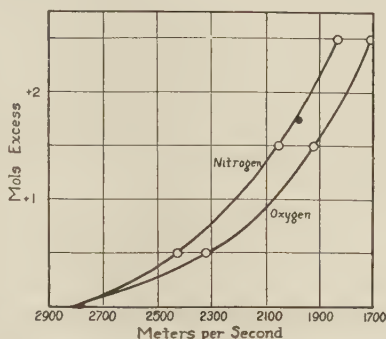


Figure 1—Effect of Excess Oxygen and Nitrogen on the Velocity of Detonation in Electrolytic Gas ($2\text{H}_2 + \text{O}_2$) (Dixon)

Table II—Effect of Nitrogen on Velocity of Flame Travel

FUEL MIXTURE	VELOCITY OF FLAME TRAVEL	REFERENCE
	<i>Cm./sec.</i>	
$\text{CH}_4 + 2 \text{O}_2$	5502.0	Payman
$\text{CH}_4 + 2 \text{O}_2 + 1.3 \text{N}_2$	1822.0	Payman
$\text{CH}_4 + 2 \text{O}_2 + 2 \text{N}_2$	967.0	Payman
$\text{CH}_4 + 2 \text{O}_2 + 6 \text{N}_2$	232.0	Payman
$\text{CH}_4 + 2 \text{O}_2 + 7.5 \text{N}_2$ (air)	93.0	Mason and Wheeler
$\text{CH}_4 + 2 \text{O}_2 + 7.74 \text{N}_2$	87.0	Mason and Wheeler
$\text{CH}_4 + 2 \text{O}_2 + 8.62 \text{N}_2$	66.0	Mason and Wheeler
$\text{CH}_4 + 2 \text{O}_2 + 9.34 \text{N}_2$	55.0	Mason and Wheeler
$\text{CH}_4 + 2 \text{O}_2 + 11.3 \text{N}_2$	36.0	Mason and Wheeler
$\text{CH}_4 + 2 \text{O}_2 + 12.6 \text{N}_2$	21.9	Payman
$2 \text{CO} + \text{O}_2$	350	Crowe and Newey
$2 \text{CO} + \text{O}_2 + 2.175 \text{N}_2$	199	Crowe and Newey
$2 \text{CO} + \text{O}_2 + 3.55 \text{N}_2$	107	Crowe and Newey

Crowe and Newey⁸ found that nitrogen decreased the velocity of flame travel in explosive mixtures of carbon monoxide and oxygen at an initial pressure of two atmospheres, as given in Table II.

Crowe and Newey also studied the effect of mixture strength on the rate of flame travel and maximum pressure developed. They found (Figure 2) that the maximum velocity of flame travel and maximum pressure were always obtained with rich mixtures of the same composition.

The maxima of both curves occur at about 40 per cent, while the theoretical mixture contains 30 per cent of carbon monoxide.

Bone, Newitt, and Townsend⁹ studied the effect of nitrogen activation in carbon monoxide-air mixtures at high pressures by photographing pressure-time curves of explosions. Their

⁷ *Ibid.*, **125**, 1957 (1924).

⁸ *Phil. Mag.*, **49**, 1112 (1925).

⁹ *Proc. Roy. Soc. London*, **103A**, 205 (1923); **105A**, 406 (1924); and **108A**, 393 (1925).

data (Table III) clearly show that nitrogen and argon, when acting as diluents, decrease the rate of rise of pressure in gaseous explosions of carbon monoxide mixtures.

The last column was calculated by dividing the maximum observed pressure by the time in seconds required for the attainment of maximum pressure. These values clearly show that nitrogen or argon, when acting as diluents, greatly decrease the rate of rise of pressure in gaseous explosions of carbon monoxide.

These conclusions are further supported by results of work carried out in a constant volume bomb similar to that described in the previous paper,¹⁰ on the effect of nitrogen as an added diluent on the rate of rise of pressure in explosions of hexane-oxygen mixtures as shown in Figure 3.

Velocity of Flame Similar to Rate of Rise of Pressure

The fact that nitrogen used as a diluent in explosive mixtures decreases the velocity of flame travel and decreases the rate of rise of pressure in all types of gaseous explosions indicates that the velocity of flame travel and rate of rise of pressure are similarly affected by diluents. The similarity between the rate of rise of pressure and the velocity of flame propagation is also evident in comparison of the work of Stevens¹¹ and the present authors' earlier work.¹² Stevens found that the velocity of flame travel varied directly as the velocity of chemical reaction, if pressure and initial temperature remained constant. The same relationship between rate of rise of pressure and rate of chemical reaction was used to explain the effect of initial temperature.¹²

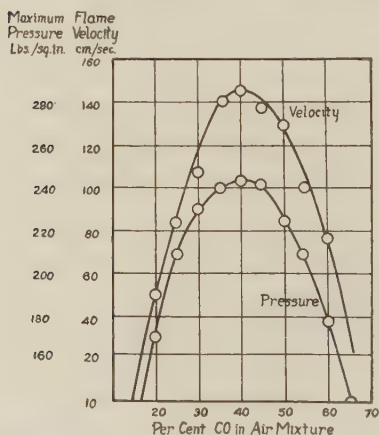


Figure 2—Effect of Mixture Strength on velocity of Flame Travel and Maximum Pressure

The similarity between velocity of flame travel and rate of rise of pressure persists even in the detonation wave. Woodbury, Lewis, and Canby¹³ state that detonation is most easily initiated in a mixture of acetylene and oxygen in the proportion to give carbon monoxide. The experimental data reported indicate that detonation was most easily initiated in mixtures containing slightly more oxygen than just necessary to form carbon monoxide and hy-

¹⁰ "Gaseous Explosions—III," *THIS JOURNAL*, **19**, 280 (1927).

¹¹ *J. Am. Chem. Soc.*, **48**, 1896 (1926).

¹² *THIS JOURNAL*, **17**, 397 (1925).

¹³ *J. Soc. Automotive Eng.*, **8**, 215 (1921).

drogen. This fact is in agreement with the data given by Dixon³ on the detonation wave propagated in explosive mixtures of ethylene and oxygen, plotted in Figure 4 and given in Table IV. These data on ethylene-oxygen mixtures are the only ones available which include a sufficient number of determinations to indicate whether or not the velocity of the detonation wave is a maximum in mixtures containing slightly more oxygen than just sufficient to form carbon monoxide and hydrogen.

Table III—Effect of Inert Gas on the Rate of Rise of Pressure, as Determined by Bone

FUEL MIXTURE	INITIAL PRES- SURE	MAX. PRESSURE RECORDED	TIME FOR MAX. PRESSURE	AV. RATE OF RISE OF PRESSURE
	<i>Atmos.</i>	<i>Atmos.</i>	<i>Sec.</i>	<i>Atmos./sec.</i>
2 CO + O ₂	4.3	43	0.0125	3440
2 CO + O ₂ + 4 A	3.0	25.5	0.035	728
2 CO + O ₂ + 4 N ₂	3.0	21.4	0.070	306

If rate of flame travel and rate of rise of pressure are related as closely as is indicated by the data reported above, it should be possible to show a maximum rate or rise of pressure in detonation waves in explosive mixtures containing slightly more oxygen than is necessary to form carbon monoxide and hydrogen.

A series of experiments were undertaken using an apparatus similar to that described in the previous paper, in which isohexane-oxygen mixtures were exploded under conditions of constant initial temperature and pressure. The data obtained are given in Table IV and plotted in Figure 4. These results in determining the rate of rise of pressure in detonating explosions of isohexane and less than theoretical oxygen are very similar to Dixon's results on the velocity of the detonation wave in ethylene-oxygen mixtures. They are of importance in indicating that the mixtures having the maximum velocity of flame propagation and the maximum rate of rise of pressure in detonation waves set up in mixtures of hydrocarbons in oxygen contain slightly more oxygen than just necessary to form carbon monoxide and hydrogen. These results are evidence in support of the conclusion that the rate of rise of pressure in gaseous explosions is influenced in the same way and by the same variables as the velocity of flame travel.

Table IV—Mixture Ratios and Velocity of Detonation Wave and of Pressure Rise

FUEL MIXTURE	VELOCITY OF FLAME TRAVEL IN THE DETONATION WAVE	FUEL MIXTURE	MAX. PRES- SURE	TIME TO DEVELOP MAX. PRES- SURE	AV. RATE OF RISE OF PRES- SURE
	<i>M./sec.</i>		<i>Lbs./ sq. in.</i>	<i>Sec.</i>	<i>Lbs./sq. in./sec.</i>
C ₂ H ₄ + O ₂	2507	C ₆ H ₁₄ + 3.5 O ₂	400	0.004	100,000
C ₂ H ₄ + 2 O ₂	2581	C ₆ H ₁₄ + 4.0 O ₂	780	0.0018	433,000
C ₂ H ₄ + 3 O ₂	2368	C ₆ H ₁₄ + 5.35 O ₂	630	0.0022	288,000
C ₂ H ₄ + 4 O ₂	2247	C ₆ H ₁₄ + 6.09 O ₂	610	0.0025	244,000

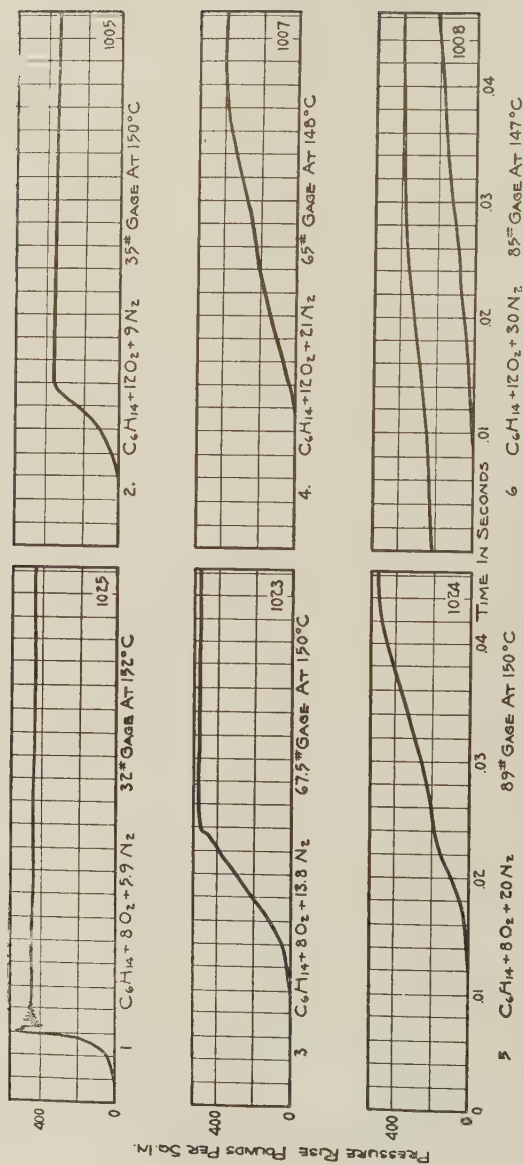


FIGURE 3—Effect of Nitrogen as an Added Diluent on the Rate of Rise of Pressure in Explosions of Hexane-Oxygen Mixtures of Constant Concentration

Further evidence of the similarity between rate of flame travel and rate of rise of pressure was given in a previous paper,¹² in which it was shown that the velocity of flame travel and the rate of rise of pressure in homogeneous explosions varied in the same way with changes in initial temperature.

Tendency to Initiate Detonation Wave Measured by Rate of Rise of Pressure

As was suggested above, the results of Dixon and Berthelot's studies reported in Table I seem to indicate that the amount of nitrogen, added as a diluent to an explosive mixture, necessary to prevent propagation of the detonation wave varies directly as the velocity of flame travel in explosive mixtures of that fuel free from nitrogen. As the rate of rise of pressure varies in the same way as the velocity of flame travel, it seems probable that the amount of diluent nitrogen required to prevent propagation of the detonation wave varies directly as the rate of rise of pressure of the explosive mixture determined under identical initial conditions. It was impossible to verify this conclusion because no adequate data on the rate of rise of pressure of different fuel mixtures were available until the research reported in the previous paper¹⁰ was completed and the tendency of these fuels to initiate the detonation was determined.

Table V—Nitrogen Necessary to Reduce Intensity of Detonation to Arbitrary Standard, and the Maximum Rate of Rise of Pressure for That Fuel

FUEL	MAX. RATE OF RISE OF PRESSURE AS DETD. IN NON-DETONATING EXPLOSIONS	PARTIAL PRESSURE ON NITROGEN
	<i>Lbs./sq. in./sec.</i>	<i>Lbs./sq. in.</i>
<i>n</i> -Hexane	47,500	16.0
<i>n</i> -Heptane	61,500	18.5
<i>n</i> -Octane	63,700	20.0
Benzene	63,000	19.0
Toluene	56,500	18.0
Xylene	47,000	16.0
Methanol	52,000	16.5
Ethyl alcohol	39,500	14.0

Accordingly, detonating theoretical mixtures of the same fuels, normal hexane, normal heptane, normal octane, benzene, toluene, xylene, methyl alcohol, and absolute ethyl alcohol, were exploded under constant initial conditions of temperature and constant density of charge as described in the previous paper,¹⁰ but with varying amounts of nitrogen added as a diluent to the explosive mixtures to eliminate the detonation wave or to reduce the intensity of the pressure rise in the detonation wave to an arbitrary standard. The results of these experiments are given in Table V, and in Figure 5 are plotted against the maximum rate of rise of pressure in slow burning mixtures ignited under constant initial conditions, as reported in the previous paper.¹⁰

As the amount of nitrogen added to the explosive mixtures was determined by means of its partial pressure indicated on a Bourdon type of gage such as is used for measuring steam pressures, these determinations do not possess a degree of accuracy equal to the determinations of the rate of rise of

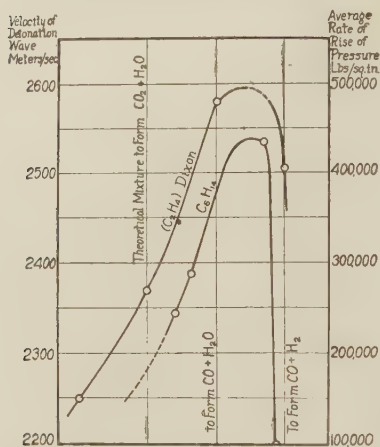


Figure 4—Effect of Mixture Ratio on Velocity of Detonation and Rate of Rise of Pressure

pressure reported in the previous paper.¹⁰ A slightly different slope of the straight line in Figure 5 may be suggested for the different types of fuels, but within the limits of experimental error a straight-line relation exists between the amount of nitrogen required to eliminate the detonation wave and the rate of rise of pressure of non-detonating explosive mixtures determined under constant initial conditions, as shown in Figure 5.

Nitrogen added as a diluent has been shown to decrease the velocity of flame travel and of rate of rise of pressure. Therefore the effect of the greater amount of diluent required to prevent detonation of fuel mixtures having a higher velocity of flame travel or rate of rise of pressure is simply to decrease this higher rate of rise of pressure. The results given in Table V and Figure 5 indicate that the rate of rise of pressure of an explosion is the major factor determining the tendency of the explosive mixtures to initiate the detonation wave, and when theoretical explosive mixtures of different fuels having the same density of oxygen and nitrogen are exploded under the same initial conditions, as described in the previous paper, the rate of rise of pressure so determined seems to be the major criterion of the tendency of that fuel to initiate the detonation wave.

The detonation wave is evident as a well-defined type of flame propagation developed directly from the flame initiated by the spark and practically independent of the surfaces of the combustion tube. Accordingly it is a homogeneous reaction because it is entirely confined to the gas phase, and a progressive homogeneous reaction because it is a homogeneous reaction which has progressed directly from the flame initiated by the spark.²

The data presented in this paper indicate that the rate of rise of pressure as measured in non-detonating theoretical explosive mixtures varies directly as the tendency of a fuel to initiate the detonation wave in a progressive homogeneous

reaction, as described. aromatic hydrocarbons have much less tendency to knock in internal combustion engines than the normal paraffin hydrocarbons having similar rates of rise of pressure. The relative tendency of the normal paraffin and aromatic hydrocarbons to initiate the detonation wave is entirely different from the relative tendency of the same fuels to knock in internal combustion engines. Therefore the detonation wave, as is recognized in progressive homogeneous reactions, is not the cause of "detonation" (fuel knock) in internal combustion engines.

But it is well known that the aro-

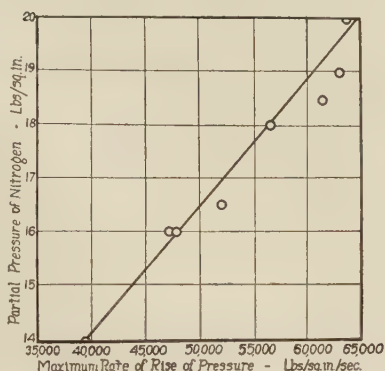


Figure 5—Partial Pressure of Nitrogen Required to Eliminate the Detonation Wave as a Function of the Rate of Rise of Pressure Determined under Constant Initial Conditions

REPRINTED FROM

Industrial *and Engineering* Chemistry

Published by the American Chemical Society

Vol. 19, No. 3

Page 366

March, 1927

Gaseous Explosions¹

V—The Probable Mechanism Causing “Detonation” in the Internal Combustion Engine

By Geo. Granger Brown and Geo. B. Watkins

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

It is well known that hot surfaces in the combustion chamber of an engine increase the tendency to “knock,” indicating that engine knock is caused by a heterogeneous reaction on the heated surfaces. It was found that if the maximum rate of rise of pressure as determined in a progressive homogeneous reaction under constant initial conditions be divided by the autoignition temperature on the absolute temperature scale, a number is obtained which varies directly as the knocking tendency of that particular fuel in an engine, or inversely as Ricardo’s “highest useful compression ratio” for that fuel.

This fact suggests rate of rise of pressure and autoignition temperature as the two factors determining the tendency of fuels to knock in an engine; and autoignition of the unburned mixture adiabatically compressed against hot surfaces as the mechanism causing “fuel knock” in an internal combustion engine.

SINCE 1905 the demand for gasoline has increased faster than the increase in production of petroleum. The petroleum refiners have therefore resorted to the most obvious means of supplying this increasing demand for their most volatile product, that of including less volatile

¹ Presented before the Divisions of Gas and Fuel Chemistry and Petroleum Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

material in the gasoline fraction. The continuation of this practice has led to poorer engine performance and particularly to a very unpleasant "knock" in the more efficient engines of higher compression ratio. This knock is metallic in sound, but is not due to mechanical impacts, as was first suggested. It was then found that retarding the spark largely eliminated this objectionable noise and the suggestion was made that the knock was due to preignition. Further experience showed that the removal of carbon from the surfaces of the combustion chamber made it unnecessary to retard the spark to eliminate this objectionable sound, which was then referred to as a "carbon knock."

During the war an intensive study was made to find more and better fuel suitable for use in the high-compression airplane engines. It was then found that some fuels would knock more readily than other fuels under the same conditions, and the "carbon knock" was rechristened the "fuel knock," as it is now known.

The knock is characterized by an intense pressure of extremely short duration and a marked decrease in the power output of the engine. The reason for this decrease in power may be explained by analogy. If it is desired to push a car or other load up a hill, the application of a steady pressure or push is more effective in moving the load than a series of impacts, such as blows from a sledge, in which the pressure developed is many times that exerted by the steady pressure, but of such short duration that no work is accomplished. Similarly with the explosion in an internal combustion engine if it exerts a steady pressure on the piston by normal combustion, the maximum power will be developed; if the explosion knocks, a large part of the potential energy is spent in developing an intense momentary pressure which does not persist long enough to do work or develop power.

Continued research on the fuel knock seemed to indicate that some of its characteristics were similar to those possessed by the "detonation wave" set up in a progressive homogeneous reaction, previously discovered and investigated by Berthelot,^{1,*} LeChatelier,² and Dixon.³ Accordingly the fuel knock is referred to as "detonation," and some investigators⁴ go so far as to assume that the fuel knock is due to initiation of a true detonation wave such as occurs in progressive homogeneous reactions.

A number of different theories have been advanced to explain the cause of the intense pressure rise which is evident by the metallic click, "knock," or "pinking" referred to as detonation. It is universally agreed that the intense pressure is the cause of the sound or knock. The mechanism of the combustion which develops the intense pressure is the point of difference and is becoming a popular subject for debate.

Experimental work of many investigators concerning the influence of initial conditions and fuel constitution on detona-

* Numbers in text refer to bibliography at the end of the article.

tion in engines and in progressive homogeneous explosions has established a number of important facts which must be considered in any adequate discussion of this subject. For the sake of clearness and convenience these facts are listed in the following outline:

A—An increase in the initial temperature (except in mixtures containing an excess of fuel and below 75° C.):

a—Decreases the velocity of the detonation wave set up in gaseous explosions in long tubes³ (progressive homogeneous explosions).

b—Decreases the rate of flame propagation in progressive homogeneous explosions in cylindrical bombs.⁶

c—Decreases the rate of rise of pressure in gaseous explosions in spherical and cylindrical bombs^{6,7} (progressive homogeneous explosion).

d—Decreases the tendency to initiate the detonation wave in cylindrical bombs^{5,7} (progressive homogeneous reactions).

e—Increases the tendency to knock ("detonate") in internal combustion engines.^{4,8,9,10}

f—Increases the tendency to initiate autoignition of the unburned gases ahead of the flame in bomb explosions⁸ (compound homogeneous or hetero-homogeneous explosion.¹¹)

B—An increase in initial pressure:

a—Increases the velocity of the detonation wave.³

b—Increases the rate of rise of pressure in bomb explosions.^{7,12,13,14}

c—Increases the tendency to initiate the detonation wave in bomb explosions.⁵

d—Increases the tendency to initiate engine knock. This is evident in all aircraft engines where it is the universal experience that the knock decreases with increasing altitude.¹⁵

C—The addition of diluents:

a—Decreases the velocity of the detonation wave.^{3,5}

b—Decreases the velocity of flame travel before the detonation wave is initiated.^{16,17,18,19}

c—Decreases the rate of rise of pressure in bomb explosions.^{12,20}

d—Decreases the tendency to initiate the detonation wave.^{3,20}

e—Decreases the tendency to initiate engine knock.^{8,15}

D—Surface conditions of the combustion chamber:

a—Have no effect on the velocity of the detonation wave set up in long tubes,^{1,3,21}

b—Have a pronounced effect on the engine knock:

1—The presence of carbon deposits increases the tendency to knock.¹⁰

2—The presence of hot surfaces increases the tendency to knock.^{9,10,22} The elimination of hot surfaces in the combustion chamber largely prevents knocking.²³

The fact that surface conditions and surface temperatures have a very important effect on engine knock indicates that the combustion causing the knock takes place or is initiated in the gas-solid interface, as on an exhaust valve or other highly heated surface. Such a reaction taking place in the gas-solid interface is a heterogeneous reaction by definition.¹¹

The fact that an increase in initial temperature decreases the rate of rise of pressure and the tendency to set up the detonation wave in progressive homogeneous reactions, but has the opposite effect on engine knocking, is further evidence

that the mechanism of the reaction causing the engine knock is entirely different from that of the progressive homogeneous reaction of the detonation wave.

Initial pressure has the same effect upon homogeneous reactions as upon heterogeneous reactions involving gases, as an increase in pressure increases the concentrations or activities of the reacting gases in both cases.

Likewise the addition of diluents affects homogeneous reactions in the same way as heterogeneous reactions. Accordingly the fact that these two variables, the initial pressure and the addition of diluents, have the same effect on bomb explosions and engine knock is of no moment in determining differences in the mechanism of the two reactions.

The facts reviewed above indicate that the engine knock is caused by a reaction entirely different from the progressive homogeneous reaction of the detonation wave, and the effect of surface conditions indicates that the engine knock is caused by a heterogeneous reaction on the heated surfaces of the combustion chamber. If the engine knock is caused by autoignition of the unburned gas on heated surfaces ahead of the flame initiated by the spark, the intensity of the knock will depend largely upon the amount of unburned mixture present when autoignition is developed.

If the explosion initiated by the spark has a high rate of rise of pressure, the unburned mixture will be compressed more rapidly and will develop autoignition with a greater amount of unburned fuel present, than if the explosive mixture had a low rate of rise of pressure. If the fuel mixture has a low autoignition temperature, autoignition will occur earlier and with a greater amount of unburned fuel present than if the autoignition temperature is high. Assuming the simplest relationship between these two factors, the amount of unburned fuel present when autoignition occurs, and therefore the intensity of the knock, will be directly proportional to the rate of rise of pressure of the exploding mixture, in a progressive homogeneous reaction, and inversely proportional to the autoignition temperature of the fuel.

The rate of rise of pressure of explosive mixtures of a number of fuels has been determined and reported in a previous paper.²⁴ A survey of the literature shows poor agreement on the data of autoignition temperatures of gaseous and liquid fuels as determined by different investigators and with different types of apparatus.

Moore²⁵ determined the autoignition temperature of a number of liquid fuels including most of those used in this investigation, by means of the "spontaneous ignition meter," which consisted of a block of steel with a base deeply grooved to furnish a greater heating surface to the burner flame. In the center of the upper surface a hole was machined exactly to fit a nickel or platinum crucible. A cover screwed to the top of the block was provided with two small holes for the oxygen or air inlet and for the admission of the substance to

be tested. The oxygen or air was passed through holes in the casting, so that it entered the crucible at the temperature of the diffusion block. The block was provided with a hole to fit the hot junction of a thermocouple used to indicate the temperature of the instrument.

The available data on the autoignition temperatures of the fuels used in this investigation are given in Table I.

Table I—Autoignition Temperatures

FUEL	AUTO- IGNITION TEMPERATURE	INVESTIGATOR	APPARATUS
	° C.		
Hexane + O ₂	287	Moore ²⁵	Spontaneous ignition meter
Heptane + O ₂	281	Moore ²⁵	Spontaneous ignition meter
Pure benzene + O ₂	620	Moore ²⁵	Spontaneous ignition meter
Toluene + O ₂	596	Moore ²⁵	Spontaneous ignition meter
Xylene + O ₂	484	Moore ²⁵	Spontaneous ignition meter
Methanol + O ₂	506	Moore ²⁵	Spontaneous ignition meter
Ethyl alcohol + O ₂	395	Moore ²⁵	Spontaneous ignition meter
Ethyl ether + O ₂	190	Moore ²⁵	Spontaneous ignition meter
Heptane + air	280	Tizard and Pye ²⁶	Compression method
Pure heptane	245	Ormandy ²⁷	Spontaneous ignition meter
Absolute ethyl alcohol and air	510	Holm ²⁸	
Absolute ethyl alcohol and air	465	White and Price ²⁹	Glass tube
Ethyl ether and air	187	White and Price ²⁹	Glass tube
Ethyl ether and air	227	Tizard and Pye ²⁶	Compression method
Ethyl ether and air	190	Alilaire ³⁰	
Ethyl ether and air	400	Holm ²⁸	
Ethyl ether and air	1033	McDavid ³¹	Soap-bubble method
Ether 5% and air	907-1068	White and Price ²⁹	Soap-bubble method
Ether 12% and air	859-1035	White and Price ²⁹	Soap-bubble method
Benzene 51% in air	1075-1025	White and Price ²⁹	Soap-bubble method

Moore's data on the autoignition temperatures are used for this comparison, because they are the only set of values for the fuels available, and not because they are thought to be most accurate. However, all of these determinations were made by the same investigator and in the same apparatus and therefore should be relative at least.

In Table II the maximum rate of rise of pressure as given in a previous paper,²⁴ is repeated in column 2, and the autoignition temperature as determined by Moore²⁵ is given on the absolute temperature scale in column 3. The relative knocking tendency as estimated by the product of the rate of rise of pressure and the reciprocal of the absolute autoignition temperature (obtained by dividing the rate of rise of pressure as given in column 2 by the autoignition temperature as given in column 3) is given in column 4. The highest useful compression ratio as determined by Ricardo⁵ is given in column 5. As the knocking tendency varies inversely as the highest useful compression ratio, it should be possible to estimate the highest useful compression ratio of any fuel by using the inverse ratio of the data given in column 4 and

the highest useful compression of one fuel. The highest useful compression ratio estimated in this way, using the highest useful compression ratio of toluene as 7, for a basis of comparison, is given in column 6.

Table II—Knocking Tendency as Determined by Rate of Rise of Pressure and Autoignition Temperature

(1)	(2)	(3)	(4)	(5)	(6)
FUEL	MAX. RATE OF RISE OF PRESSURE ²⁴	AUTO IGNITION TEMPER- ATURE (MOORE) ²⁵	COLUMN (2) DIVIDED BY COLUMN (3)	RICARDO'S ⁸ HIGHEST USEFUL COM- PRESSION RATIO	ESTIMATED HIGHEST USEFUL COMPRESSION RATIO
	<i>Lbs./sq. in./sec.</i>	<i>° K.</i>			
<i>n</i> -Hexane	47,500	560	84.8	80% hexane 5.1	5.36
<i>n</i> -Heptane	61,500	554	110.8	97% heptane 3.75	4.1
<i>n</i> -Octane	63,700	548 ^a	116.0	...	3.9
Benzene	63,000	893	70.5	6.9 ^b	6.45
Toluene	56,500	869	65.0	99% toluene >7	7.0
Xylene	47,000	757	62.2	>7	7.3
Methanol	52,000	779	66.7	5.2 ^b	6.8
Ethyl alcohol (absolute)	39,500	668	59.1	98% ethyl alcohol 7.5	7.7
Amyl alcohol	48,000				

^a This value for octane was estimated and not determined by Moore.

^b Preignition occurred before audible detonation.

Although the estimated highest useful compression ratio is not in absolute agreement with the highest useful compression ratio as determined by Ricardo, considering the different sources and purity of the fuels used, the agreement between the estimated and experimentally determined values for the highest useful compression ratio is surprisingly good and justifies the hypothesis that the tendency of fuels to knock in internal combustion engines is determined by two factors, the rate of rise of pressure and the autoignition temperature. The important effect of hot surfaces on engine knocking suggests that the mechanism of combustion during engine knocking is complex and composed of a progressive homogeneous reaction initiated by the spark, followed by a heterogeneous reaction initiated by autoignition of the unburned part of the mixture that is compressed against the hot surface by the progressive reaction initiated by the spark.

This conception of the mechanism of engine knock is very similar to that suggested by Ricardo,³² who says,

Broadly speaking, it would appear that two factors determine whether or not a fuel will detonate:

- 1—The self-ignition temperature of the fuel-air mixture.
- 2—The rate of acceleration of burning as the ignition temperature is exceeded.

If "the rate of acceleration of burning" is interpreted to mean "the rate of rise of pressure," the data here presented confirm Ricardo's earlier statement.

Practically the same mechanism was suggested as the cause of engine knock by Woodbury, Lewis, and Canby,⁵ based on their experience with bomb explosions:

It is our feeling, however, that information at hand favors more strongly the theory of autoignition of the high-density gases ahead of the flame front than that of detonation (the detonation wave).

Different suggestions concerning the mechanism of engine knock have been advanced by many investigators. Among the more important of these is the theory that the engine knock is caused by a true detonation wave similar to that recognized as a progressive homogeneous reaction in long tubes or bombs. This theory was supported by Midgley,⁴ who gave the following reasons for his certainty that gaseous detonation (the detonation wave) within the engine cylinder is the phenomenon that causes engines to knock:

1—A high-pressure, high-velocity detonation wave striking the cylinder head should distort it and thereby produce the metallic noise that is called a knock.

2—The luminosity that is observable during gaseous detonation in an explosion tube is also present in the flame within the cylinder when the engine knocks.

3—Antiknock materials, such as diethyl selenide and tetraethyl lead, could scarcely affect the autoignition temperature of a fuel when used in the very small quantities that are necessary to suppress knocking. Apparently, the only way to explain their effect is on the basis that they affect the constant of the reaction velocity of gaseous detonation. Further, these materials will suppress the detonation occurring in explosion tubes to the same degree and in the same manner that they suppress the knock in engines.

These three facts, although true in themselves, are inadequate to support the conclusion that the engine knock is due to the true detonation wave. The metallic noise called a knock might be caused by any intense rapid rise in pressure within the cylinder such as is developed when autoignition occurs.⁵ The luminosity is caused by glowing particles of carbon accompanying combustion at high pressure as is known to exist in either autoignition or detonation. Antiknock materials may affect the rate of reaction in the way suggested by Midgley, and accordingly decrease the rate of rise of pressure and tend to prevent engine knocking, without effect on the autoignition temperature. These facts are in complete harmony with the suggestion made above, that the engine knock is due to some form of autoignition and depends upon the two factors, rate or rise of pressure and autoignition temperature. Furthermore, in support of his contention, Midgley assumes that the detonation wave is more readily set up in mixtures at higher initial temperatures. This is contrary to experimental fact.^{3,5,7} But an increase in initial temperature is known to increase the tendency to initiate autoignition.⁵ If the engine knock were decreased by an increase in initial temperature, a true detonation wave, or rate of rise of pressure without involving autoignition, could then be suggested as the probable cause of the engine knock. These conditions have been observed in cold engines free from hot surfaces in the combustion chamber, but usually

an increase in the initial temperature increases the engine knock, which cannot then be accounted for by a detonation wave.

Tizard³³ suggests that the knock in an internal combustion engine "occurs when the rate of rise of pressure exceeds a certain unknown amount." He doubts that the knocking is caused by a true detonation wave, and treats his suggestion that the rate of rise of pressure is the factor determining detonation as "a comparatively secondary consideration and if one accepts the view that the rate of combustion increases rapidly with the temperature, either theory would lead to the conclusion that 'knocking' will only occur if, some time before combustion is complete, the whole or part of the gas exceeds a certain temperature"—or "if the maximum flame temperature exceeds a certain temperature, which is characteristic of the fuel."

Tizard bases his deductions on the assumptions "that the rate of combustion increases rapidly with the temperature" and that rate of combustion is equivalent to rate of rise of pressure. It has been shown that an increase in initial temperature decreases the velocity of flame travel,⁵ and the rate of rise of pressure,^{6,7} in homogeneous reactions. Accordingly, if the rate of combustion is equivalent to rate of rise of pressure, as in Tizard's second assumption, the rate of combustion cannot increase with increasing temperature as he has assumed.

As pointed out by Alcock,¹⁵ Tizard's theory that knocking occurs only when the whole or some part of the unburned charge exceeds a certain temperature characteristic of the fuel, is inadequate to explain the fact that a decrease in initial pressure, as in the case of an aircraft engine at high altitude, decreases or eliminates the engine knock, because the maximum temperature of combustion is the same except for slight relative changes in the jacket losses.

In brief, Midgley and Tizard have overlooked the fact that an increase in initial temperature decreases the rate of rise of pressure of a homogeneous gaseous explosion and have assumed the opposite to be true. This led Midgley to ignore the importance of the autoignition temperature and Tizard to ignore the importance of the rate of rise of pressure. The facts summarized in this paper indicate that both the rate of rise of pressure and the autoignition temperature must be considered in estimating the tendency of a fuel to knock in an internal combustion engine, and suggest autoignition of the unburned part of the charge caused by adiabatic compression against heated surfaces as the mechanism of combustion causing engine knock. The rate of flame travel and the rate of rise of pressure in the explosions following autoignition may approach the rates accompanying the detonation wave, but the mechanism of autoignition is so radically different from the mechanism initiating the detonation wave that a precise distinction should be made.

Bibliography

- 1—Bertholet, *Compt. rend.*, **93**, 18 (1881).
- 2—LeChatelier, *Ibid.*, **93**, 145 (1881).
- 3—Dixon, *Trans. Roy. Soc. London*, **184A**, 97 (1893).
- 4—Midgley and Janeway, *J. Soc. Automotive Eng.*, **12**, 367 (1923).
- 5—Woodbury, Lewis, and Canby, *Ibid.*, **8**, 209 (1921).
- 6—Nägel, *Mitt. Forschungsarbeiten*, **54**, 1 (1908).
- 7—Brown, Leslie, and Hunn, *Ind. Eng. Chem.*, **17**, 397 (1925).
- 8—Ricardo, *Automobile Eng.*, **11**, 130 (1921).
- 9—Hollaway, Huebotter, and Young, *J. Soc. Automotive Eng.*, **12**, 111 (1923).
- 10—Young and Hollaway, *Ibid.*, **14**, 315 (1924).
- 11—Brown, *Ind. Eng. Chem.*, **17**, 1229 (1925).
- 12—Bone, Newitt, and Townsend, *Proc. Roy. Soc. (London)*, **103A**, 205 (1923).
- 13—Bone, Newitt, and Townsend, *Ibid.*, **105A**, 406 (1924).
- 14—Bone, Newitt, and Townsend, *Ibid.*, **108A**, 391 (1925).
- 15—Alcock, *Automobile Eng.*, **14**, 165 (1924).
- 16—Mason and Wheeler, *J. Chem. Soc.*, **111**, 1044 (1917).
- 17—Payman, *Ibid.*, **117**, 48 (1920).
- 18—Campbell and Ellis, *Ibid.*, **125**, 1957 (1924).
- 19—Crowe and Newey, *Phil. Mag.*, **49**, 1112 (1925).
- 20—Brown and Watkins, *Ind. Eng. Chem.*, **19**, 363 (1927).
- 21—Wendlandt, *Z. physik. Chem.*, **110**, 673 (1924); **116**, 277 (1925).
- 22—Horning, *J. Soc. Automotive Eng.*, **13**, 144 (1923).
- 23—Abell, *Ibid.*, **13**, 301 (1923).
- 24—Brown and Watkins, *Ind. Eng. Chem.*, **19**, 280 (1927).
- 25—Moore, *Automobile Eng.*, **10**, 199 (1920).
- 26—Tizard and Pye, *Phil. Mag.*, **44**, 79 (1922).
- 27—Ormandy, *J. Inst. Petroleum Tech.*, **10**, 335 (1924).
- 28—Holm, *Z. angew. Chem.*, **26**, 273 (1913).
- 29—White and Price, *J. Chem. Soc.*, **115 II**, 1462, 1248 (1919).
- 30—Alilaire, *Compt. rend.*, **168**, 729 (1919).
- 31—McDavid, *J. Chem. Soc.*, **111**, 1003 (1917).
- 32—Ricardo, *Automobile Eng.*, **12**, 265 (1922).
- 33—Tizard, *N. E. Coast. Inst. Eng. Shipbuilders, Trans.*, **37**, 381 (1921).

